

Anisotropic charge transfer between hydrogenic states and a metallic substrate

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By measuring the angular distribution of photon emission from desorbed excited atoms it is possible to measure the anisotropy in charge-transfer rates between metallic states and the oriented excited states outside of the surface. The measured anisotropy of 2.5 shows excellent agreement with the calculated value of 2.54 and clearly demonstrates that intra-atomic correlation effects must be taken into account when describing charge transfer.

A knowledge of charge transfer is important in developing an understanding of a number of dynamical processes near surfaces.¹ Such processes include dissociation, adsorption, and the desorption of ions and excited atoms. The same mechanism will also influence the relative decay channels in the electronic structure probes, ion neutralization spectroscopy, and metastable atom deexcitation spectroscopy. Several papers² have suggested that the charge-transfer rates will be dependent on whether the relevant orbital is aligned parallel or perpendicular to the surface, a reflection of the different overlap between the metallic states and the atomic state located outside of the surface. In this paper we are able to show that such an anisotropy in charge transfer does indeed exist. By measuring the intensity of Lyman α radiation emitted from excited hydrogen atoms desorbed from an alkali-covered surface, we are able to determine the relative charge-transfer rates for $2p$ orbitals aligned parallel or perpendicular to the surface.

The hydrogen atoms are desorbed from a copper (001) surface with various cesium coverages up to saturation. By examining the photon-emission angle we find that for desorption from the completed Cs monolayer coverage the charge-transfer rates favor transitions into p orbitals aligned perpendicular to the surface over those aligned parallel by a factor of approximately 2.5. From coverages corresponding to the maximum change in the work function the relative charge-transfer rates are, within the accuracy of the experiment, equal.

The basic experimental approach has been described elsewhere.³ Briefly, hydrogen atoms are desorbed from an alkali-covered surface following excitation by an incident electron beam. In the present study the incident electron beam energy was typically 30 eV and the incident beam current densities were of the order of $0.8 \mu\text{A}/\text{mm}^2$. Cesium was evaporated onto a copper (001) surface from an SAES getter and hydrogen subsequently adsorbed. No ordered structures were observed for the Cs overlayers in this study. Photons emitted by the desorbed excited hydrogen atoms were detected by a normal-incidence spec-

trograph described in detail elsewhere.⁴ The photon intensity was measured as a function of emission angle by varying the angle subtended by the surface normal of the sample with the axis of the spectrograph. However, because the sample is rotated in this manner it is necessary to normalize the data to account for the different surface area exposed to the incident electron beam. With a fixed angle of 45° between the spectrograph and the incident electron direction this normalization factor is simply $(\cos\phi + \sin\phi)$ where ϕ is the angle of photon emission with respect to the surface normal. The angular acceptance of the spectrograph for this study was $+/-4.5^\circ$. All experiments reported in this paper were carried out with the sample at room temperature.

Figure 1 shows typical photon spectra obtained from the saturated Cs coverage following exposure to 5 L [1 langmuir (L) = 10^{-6} Torr s] of hydrogen with substrate at room temperature. The peak associated with Lyman α emission from desorbed hydrogen atoms is clearly seen at 10.2 eV. At a Cs coverage of one monolayer the film is essentially metallic and the energy shifts of the excited hydrogen levels will reflect the metallic character. Using the retarding potential method we find that the work-function change from the clean surface at this coverage is -2.7 eV corresponding to a work function of 1.9 eV, the clean surface work function of Cu(001) being 4.6 eV.⁵ Thus the higher excited levels will therefore always be above the Fermi level and will not be available for the formation of excited atoms through the resonance process.

The peak at 11.2 eV in Fig. 1 represents the radiative decay of the Cs $5p$ level. The angular dependence of this latter emission shows a dependence on the thickness of Cs and will be discussed in more detail elsewhere.⁶ Unlike our earlier study, no Lyman β emission is observed from this system. This may reflect a lower sticking coefficient for hydrogen and indeed the Lyman α emission is significantly lower than our earlier study.

Figure 2 shows the measured Lyman α emission intensity as a function of angles measured from the surface

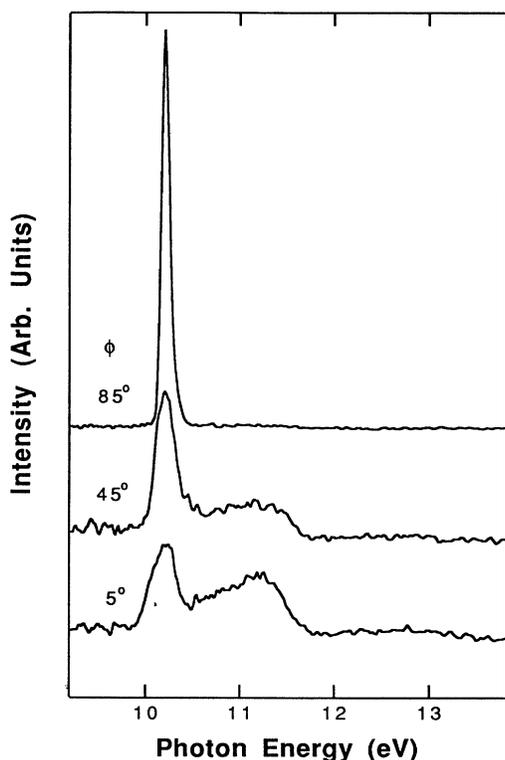


FIG. 1. Photon spectra measured as a function of the photon-emission angle determined from the surface normal. The cesium coverage for these spectra corresponds to one monolayer.

normal. The intensities represent the integrated areas in the Lyman α peaks shown in Fig. 1. As noted earlier these intensities are normalized to account for the variation in the surface area subtended by the incident beam. The figure shows results from two distinct Cs coverages, the saturated monolayer coverage and the coverage, approximately one-half saturation coverage, corresponding to the maximum change in the work function. We determine that the work functions for these two coverages are 1.9 and 1.6 eV, respectively. With subsequent exposure to hydrogen the submonolayer coverage work function increases and the monolayer coverage work function decreases. This results in the work function for the two systems being approximately the same.

Examination of Fig. 2 shows that the angular dependence of emission shows a marked change between the two regimes. At the lower submonolayer coverage the emission is isotropic with no apparent dependence on emission angles. As the Cs coverage moves towards saturation the emission starts to favor a direction perpendicular to the surface normal or parallel to the surface.

The Lyman α radiation will be emitted from a free-oriented hydrogen atom with an intensity given by $\sin^2\theta$, where θ is the angle between the photon propagation direction and the electric dipole. If we consider the radiation as emitted from a source with three perpendicular components x , y , and z with z oriented along the surface normal, the intensity measured in the yz plane will be

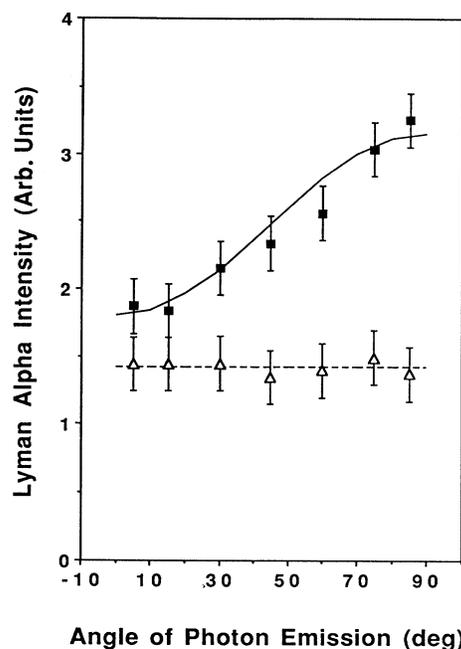


FIG. 2. The measured Lyman α intensity as a function of the angle of the photon-emission angle. The filled squares show the emission from the Cs coverage corresponding to one monolayer and the open triangles show the emission from the Cs coverage corresponding to the maximum change in the work function. The two sets of data are normalized with respect to each other.

given by

$$n_x + n_y \cos^2\phi + n_z \sin^2\phi . \quad (1)$$

Here n_x , n_y , and n_z are the relative occupations of the three components and ϕ is, as before, the angle measured with respect to the surface normal. We assume that the two components n_x and n_y parallel to the surface are equal, n_{\parallel} , and look for the ratio $R = n_z/n_{\parallel}$ relating the perpendicular and parallel components. A value of one for R corresponds to equal occupations with resulting isotropic emission. The dashed and solid lines in the figure show fittings to the two experimental observations with R having a value of 1.0 and 2.5, respectively.

The experimentally observed anisotropy of the tunneling rates of the different $H(n=2)$ states can be understood from the results of recent theoretical investigations of the shift and broadening of hydrogen levels near metal surfaces *using a complex scaling method*.⁷⁻⁹

The interaction between a hydrogen atom and a metal surface results in a hybridization of the excited states of the atom.⁶ The $H(2s)$ and $H(2p_z)$ orbitals hybridize and form a short-lived state, Ψ_2^+ oriented towards the surface and a long-lived state, Ψ_2^- oriented towards the vacuum direction. Outside a smooth metal surface, the $H(2p_{x,y})$ states remain degenerate and will be denoted Ψ_2^0 . The widths of Ψ_2^0 are intermediate between the Ψ_2^+ and Ψ_2^- states.

For a hydrogen atom outside a clean metal surface, all hydrogen levels shift upwards with decreasing atom-surface separation. This upshift is due to the image po-

tential and has been discussed elsewhere.⁷ If electropositive impurities such as alkali atoms are present on the surface, strong dipolelike fields will be induced. These fields induce a strong downshift of the $H(n=2)$ levels in the vicinity of the alkali atom.^{3,8}

At the cesium coverage corresponding to the minimum work function, the cesium atoms are partly ionized. The energy shift of the hydrogen levels is therefore similar to the shifts outside an electropositive impurity atom. Close to the surface the states will therefore be downshifted. Since the work function is 1.75 eV, the different $H(n=2)$ states will lie below the Fermi energy for all hydrogen-surface separations. The population of the H states will therefore not change during the outgoing trajectory and the final-state population of the desorbing H is the same as the initial distribution of the H levels generated by the electron stimulating the desorption. In a previous investigation we found that the electron populates the different H levels with equal probability. The ratio of the population of $m=0$ and ± 1 states is therefore unity.³

At the high Cs coverage, the situation is very different. The surface is now metallic and the neutral hydrogen levels are upshifted close to the surface. Once formed by the excitation process, these states will therefore ionize rapidly. A less probable but competing process will be the formation of the negative ion state. This state is downshifted close to the surface and decays into $H(1s)$ by resonant tunneling at distances larger than 7 a.u. from the surface.¹⁰ Since neither the negative ion state nor the $H(1s)$ can emit Lyman α radiation the discussion can be restricted to the $H(n=2)$ states formed by resonant neutralization of the desorbing protons. At a distance of around 5 a.u., the different $H(n=2)$ states shift below the Fermi energy. The various $H(n=2)$ states can then be populated by resonant tunneling. Since the Ψ_2^+ state has the largest width, charge transfer will predominantly occur in this state. However, since several levels are involved in the charge transfer, proper consideration must be taken to describe intra-atomic correlation effects.⁹ The intra-atomic correlation prevents more than one state from being populated so that for an atom with N excited levels

$$n^{\text{tot}} = \sum_i^N n_i(t) \leq 1. \quad (2)$$

In the absence of intra-atomic correlation this would be $n^{\text{tot}} \leq N$.

The dynamics can be described using a time-dependent multiple-level Anderson model. Recently it has been shown that the population of the different levels can be obtained by the solution of a set of equations⁹ of the form

$$\frac{dn_2^i(t)}{dt} = -\Gamma_2^i(t)\{1-f[\epsilon_2^i(t)]\}n_2^i(t) + 2\Gamma_2^i(t)f[\epsilon_2^i(t)][1-n^{\text{tot}}(t)], \quad (3)$$

where i represents $+$, 0 , and $-$. In these equations, $n_2^+(t)$, $n_2^0(t)$, and $n_2^-(t)$ are the instantaneous occupations of the different $H(n=2)$ states and $n^{\text{tot}}(t) = n_2^+(t) + n_2^0(t) + n_2^-(t)$. The factor of 2 in front of the second term, the gain term, accounts for spin de-

generacy. Again, in the absence of intra-atomic correlation the last factor in Eq. (3), $[1-n^{\text{tot}}(t)]$, would be replaced by $[1-n_2^i(t)]$. The splittings between the different $H(n=2)$ levels are much smaller than their widths so the levels are assumed degenerate. The energies ϵ_2 and widths Γ_2^i have been calculated as a function of position outside of the metal surface⁷ and $f(\epsilon)$ is the Fermi-Dirac function. We assume that the H motion is perpendicular to the surface with a constant perpendicular velocity corresponding to 1-eV kinetic energy. The work function is assumed to be 2 eV. In Fig. 3, the calculated energy level ϵ_2^+ , widths Γ_2^i , and instantaneous populations $n_2^i(t)$ of these levels are plotted during the trajectory. When the hydrogen levels cross the Fermi energy at a distance of 5.5 a.u. from the surface, the $n=2$ levels can be populated by resonant tunneling. Since the tunneling rate into the Ψ_2^+ state is largest, the population of this state increases faster than the population of the more long-lived Ψ_2^0 and Ψ_2^- states. At a distance of 5.7 a.u., the total population of the $n=2$ levels is 1 and the intra-atomic correlation prevents further tunneling of electrons into the hydrogen atom. The final-state populations $n_2^+(t) = 0.69$, $n_2^-(t) = 0.02$, and each $n_2^0(t) = 0.14$. The Ψ_2^+ state consists of equal parts of $H(2s)$ and $H(2p_z)$. The Lyman α radiation is emitted solely from the transition $H(2p \rightarrow 1s)$ resulting in an anisotropy ratio $R = 2.54$.

The results of these calculations do not depend sensitively on velocities nor on the substrate that was used to calculate the widths. The crucial parameters are the anisotropies between the various $H(n=2)$ states. Since the $H(n=2)$ states are formed very fast, the anisotropy ratio

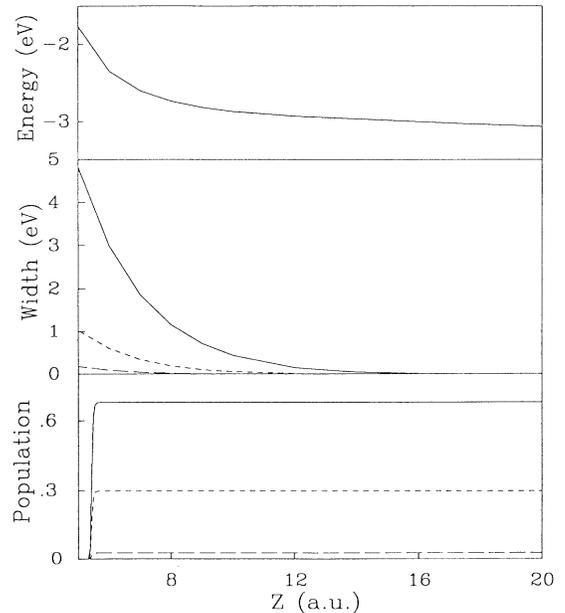


FIG. 3. The binding energy ϵ_2^+ , widths Γ_2^i , and instantaneous populations $n_2^i(t)$ of the different $H(n=2)$ levels as a function of atom-surface separation. The solid line refers to the Ψ_2^+ state, the dotted line is the Ψ_2^0 states, and the dashed lines refer to the Ψ_2^- state.

is simply given by

$$r(z) = \frac{\Gamma_2^+(z) + \Gamma_2^-(z)}{2\Gamma_2^0(z)} \quad (4)$$

at the position z_0 where the levels cross the Fermi level. These tunneling-rate anisotropies are determined by the spatial orientation of the hybridized atomic states. While the absolute magnitude of the widths of these states is sensitive to the details of the surface potential, the ratio of the widths of the different states are almost the same for all metallic substrates. Since $r(z)$ only varies weakly with distance, i.e., $r(5)=2.44$, $r(6)=2.57$, $r(7)=2.79$, the result does not sensitively depend on the crossing distance. The experimentally determined ratio R and the calculated $r(z)$ will be the same quantity only in the limit of infinitesimally small velocities for the excited atoms and only at the point where the excited level crosses the Fermi level.

In the calculations of the final population of the $H(n=2)$ states, it was crucial to include the effects of

intra-atomic correlation. If this effect had been neglected, all the $H(n=2)$ states would have been fully populated resulting in an anisotropy ratio of $R=1$.

In summary we have therefore demonstrated that anisotropies in charge-transfer rates between metallic states and oriented states outside of the surface can be determined by measuring the angular distribution of photon emission from desorbed excited atoms. The measured anisotropy of approximately 2.5 shows excellent agreement with the calculated value of 2.54 and clearly demonstrates that intra-atomic correlation effects must be taken into account when describing charge transfer between almost degenerate levels and surfaces.

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